Aerojet Solid Propulsion Company

19 January 1989

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

Attention: Dr. R. S. Miller (Code 1132P)

Subject: Fifth Quarterly Summary of Progress on Contract
"Energetic Thermoplastic Elastomer Synthesis"
Covering Period 01 September 1988 to 30 November 1988
Contract No. N00014-87-C-0098

Dear Dr. Miller:

Work has continued during reporting period on the synthesis of triblock polymers comprising of the BAMO-AMMO-BAMO structure. We have synthesized polymers for NWC's effort to elucidate structure and resolve the structure/property relationship. As required structures have been requested, we have supplied the appropriate sample. This has included homo polymers as well as di- and tri-blocks. We have also supplied the University of Massachusetts with multiple half pound quantities of each homo polymer to support their blocklinking efforts. Each of these investigators will report the results of their work separately.

One question that we had not addressed earlier in the program has now been examined. Using the BCC/ASF initiator, we have extensively used the 1:2 MOL ratio as theoretically required. But this assumes that we can accurately weigh out 100% pure materials and maintain the ratio to the point of initiation. We have now evaluated other ratios between 1:1.5 and 1:3. Initial observation in our laboratories is that no deleterious effect is noted at ratios above theoretical and that, for practical purposes, there is a definite advantage in using a slight excess of ASF (ASF is extremely moisture/air sensitive). Samples of these polymers (homo BAMO) have been supplied to NWC to gauge any structural changes brought about by adjusting this initiator ratio. Definitive results are not yet available from them.

One area of concern during this past contract year is the inability to achieve greater than 80% blocking during the systematic addition. Even though 100% of the AMMO is polymerized into a homo AMMO structure, approximately 15-25% of the final polymer contains homo AMMO. This obviously points to some termination of the AMMO growing end, either during propagation with AMMO or at the onset of addition of BAMO. During this reporting period, a fortuitous polymerization lead us to understand and probably resolve the problem. Using a freshly prepared batch of AMMO, we suddenly found, for the first time, that we could not induce polymerization using ASF/DCC. Reverting back to an old batch of AMMO, no problems were encountered with the catalyst. Therefore, we deduced that there was something wrong with this batch of AMMO. GC and water content analysis showed it to be well within our required specifications. In

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fact the water content was the lowest we had ever recorded. Nevertheless, there was something different. As we could detect no difference by standard techniques, we examined this batch of monomer by capillary gas chromatography. Using a HP-1 methyl silicone gum (10M x 0.53mm x 2.65μm film thickness) column and flame ionization detector, we were able to detect 0.3% of a low boiling component that was not present in a batch of AMMO that underwent rapid polymerization. This peak was quickly assigned to be residual dimethyl formamide from the azidification step. Analysis of previous batches of AMMO and BAMO showed a direct relationship between the presence of trace amounts of DMF and the lack of completion of the polymerization. In fact, this latter batch of AMMO with 0.3% DMF contained (on a Mol basis) more DMF than ASF catalyst, and it did not undergo initiation. This would suggest that DMF quenches the initiation. To prove the point we washed this batch of AMMO with water and totally removed the DMF. After this treatment the AMMO polymerized easily.

Examining the analysis of previously used AMMO and BAMO, the results indicate that BAMO usually contained residual DMF (0.05 to 0.2%) and it seems likely that the homo AMMO content of the polymer is due to DMF quenching at the start of addition of the BAMO stream. The mechanism of this quenching is obscure at this time and probably not important. In the future we will make certain that all monomers are completely devoid of any DMF prior to polymerization. This can be easily achieved by water washing.

Participating Personnel: R. W. Fletcher, H. W. Cheung

Respectfully submitted,

G. E. Manser
Scientist
Chemical Research and Development

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cc Phillip Miller, Consultant

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